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(54) PRODUCTION OF WATER-ABSORPTIVE RESIN OF EXCELLENT DURABILITY

(57)Abstract:

PURPOSE: To obtain the title resin excellent in the durability and liquid permeability of a swollen gel and showing a high water absorption rate even to physiologic saline by subjecting an aqueous solution containing a water-soluble, ethylenically unsaturated monomer, a crosslinking agent and a water-soluble chain transfer agent each in a specified amount to aqueous solution polymerization.

CONSTITUTION: An aqueous monomer solution of a concentration of from 30wt.% to the saturation concentration containing a water-soluble, ethylenically unsaturated monomer (e.g. acrylic acid/sodium acrylate mixture), 0.005-5mol%, based on this monomer, crosslinking agent (e.g. trimethylolpropane tri-acrylate) and 0.001-1mol%, based on this monomer, water-soluble chain transfer agent (e.g. sodium hypophosphite) is subjected to aqueous solution polymerization.

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A. Relevance of the Above-identified Document

The following is a partial English translation of exemplary portions of non-English language information that may be relevant to the issue of patentability of the claims of the present application.

B. Translation of the Relevant Passages of the Document

See also the attached English Abstract.

1. Title of the invention

PRODUCTION METHOD OF WATER-ABSORBING RESIN
EXCELLENT IN DURABILITY

2. Claims

1. A production method of water-absorbing resin (D) excellent in durability, comprising: performing aqueous polymerization using a monomer (A) aqueous solution that has a concentration in the range of from 30% by weight to a saturation concentration and contains (i) water-soluble ethylene-based unsaturated monomer (A), (ii) 0.005 mol% to 5 mol% of cross-linking agent (B) with respect to monomer (A), and (iii) 0.001 mol% to 1 mol% of water-soluble chain transfer agent (C) with respect to monomer (A).

2. A production method of water-absorbing resin (F) excellent in durability, comprising cross-linking in the vicinity of a surface of water-absorbing resin (D) is cross-linked by a hydrophilic cross-linking agent that is reactive with a functional group contained in water-absorbing resin (D), which water-absorbing resin (D) is produced by aqueous polymerization performed using a monomer (A) aqueous solution that has a concentration in the range of from 30% by weight to a saturation concentration and contains (i) water-soluble ethylene-based unsaturated monomer (A), (ii) 0.005 mol% to 5 mol% of cross-linking agent (B) with respect to monomer (A), and (iii) 0.001 mol% to 1 mol% of water-soluble chain transfer agent (C) with respect to monomer (A).

3. A production method as set forth one of Claims 1 and 2, wherein water-soluble chain transfer agent (C) is hypophosphite.

4. A production method as set forth in one of Claims 1 and 2, wherein an amount of cross-linking agent (B) to be used is 0.02 mol% to 1 mol% with respect to water-soluble ethylene-based unsaturated monomer (A).

5. A production method as set forth in one of Claims

1 and 2, wherein the concentration of the water-soluble ethylene-based unsaturated monomer (A) aqueous solution is in the range of from 35% by weight to the saturation concentration.

6. A production method as set forth in one of Claims 1 and 2, wherein water-soluble ethylene-based unsaturated monomer (A) contains at least 50% of (i) acrylic acid and (ii) acrylic acid alkali metal salt and/or ammonium acid.

7. A production method as set forth in Claims 1 and 2, wherein the aqueous polymerization is performed using the water-soluble ethylene-based unsaturated monomer (A) aqueous solution in a reactor vessel having a rotation stir blade.

8. A production method as set forth in Claim 7, wherein the reactor vessel has a plurality of rotation stir blades.

9. A production method as set forth in Claim 8, wherein the reactor vessel having the plurality of rotation stir blades is a two-screwed kneader.

10. A production method as set forth in Claim 9,

wherein 0.04 mol% to 0.4 mol% of cross-linking agent (B) is used with respect to water-soluble ethylene-based unsaturated monomer (A).

11. A production method as set forth in Claim 2, wherein, in (i) 0 parts by weight to 20 parts by weight of water and (ii) 0 parts by weight to 20 parts by weight of hydrophilic organic solvent (G), 0.005 parts by weight to 5 parts by weight of at least one type of hydrophilic cross-linking agent (E) selected from compounds (E-1) containing two or more functional groups reactive with a carboxyl group and/or multivalent metal salt (E-2) is mixed and heated at a temperature of 40°C to 250°C with respect to 100 parts by weight of water-absorbing resin (D).

12. A production method as set forth in Claim 11, wherein hydrophilic cross-linking agent (E) is a compound (E-1) or compounds (E-1).

13. A production method as set forth in Claim 12, wherein the compounds (E-1) are one type or more than one type of compound selected from a polyhydroxy alcohol, a multivalent glycidylether compound, a multivalent oxazoline compound, or a multivalent amine compound.

14. A production method as set forth in Claim 11, wherein 0.5 parts by weight to 10 parts by weight of water is used with respect to 100 parts by weight of water-absorbing resin (D).

15. A production method as set forth in Claim 11, wherein 0 parts by weight to 8 parts by weight of hydrophilic organic solvent (G) is used with respect to 100 parts by weight of water-absorbing resin (D).

16. A production method as set forth in Claim 11, wherein the heating is performed at a temperature of 90°C to 220°C.

1. Detailed description of the invention
[Industrially applicable field]

The present invention relates to a production method of a water-absorbing resin excellent in durability. Specifically, the present invention relates to a production method of a water-absorbing resin that: has excellent absorbency; has excellent absorption rate; has excellent durability after having swelled; can form a swelled gel that is less sticky; and has excellent liquid permeability.

Such water-absorbing resin can be produced inexpensively and easily. Furthermore, the water-absorbing resin is excellent in safety and absorption

power. Therefore, the water-absorbing resin can be widely used in sanitary materials (e.g., sanitary napkins, paper diapers), in water supplying agents for agricultural activities, horticultural activities, or greenery, or in any other materials of absorbing products.

[Prior art]

In recent years, a water-absorbing resin that absorbs water of several tens to hundreds times more amount of a weight of the water-absorbing resin has been developed. Such water-absorbing resin has been widely used in various fields including, for example, a field of sanitary materials (e.g., paper diapers, sanitary napkins), a field of agriculture and forestry, and a field of civil engineering.

As a main raw material of the water-absorbing resin, for example the following materials are known: a cross-linked polymer containing partially-neutralized polyacrylic acid (Japanese Unexamined Patent Publication No. 55-84304); a hydrolysate which is a starch-acrylic graft polymer (Japanese Examined Patent Publication No. 49-43395); a saponificated vinyl acetate-acrylic ester copolymer (Japanese Unexamined Patent Publication No. 52-14689); a cross-linked hydrolyzed acrylonitril copolymer or a hydrolyzed acrylamide copolymer (Japanese Examined Patent Publication No. 53-15959); and cross-linked products thereof.

Such water-absorbing resin is demanded to exhibit,

for example, high absorbency and fast absorption rate when contacting with an aqueous liquid, and excellent suction power for absorbing liquid from a material containing the aqueous liquid.

However, depending upon the usage of the water-absorbing resin, especially durability and temporal stability (stability in terms of changes over time) of the swelled gel, in addition to the properties mentioned above, become necessary. For example, in the case where a conventional water-absorbing resin is used in sanitary materials (e.g., paper diapers), there arises a problem in that a swelled gel of the water-absorbing resin having absorbed urine is deteriorated or decomposed as time passes by. Further, in the case where a conventional water-absorbing resin is used for a long period of time in agricultural or horticultural activities, there also arises a problem in that the swelled gel of the water-absorbing resin is deteriorated or decomposed.

Examples of known methods for preventing deterioration and decomposition of the swelled gel of the water-absorbing resin include: a method wherein an oxygen-containing reducing inorganic salt or a radical chain inhibitor is contained a water-absorbing resin (Japanese Unexamined Patent Publications Nos. 63-118375 and 63-152667); a method wherein an oxidant is contained in a water-absorbing resin (Japanese

Unexamined Patent Publication No. 63-153060); or a method wherein a reductant containing sulfur is contained in a water-absorbing resin (Japanese Unexamined Patent Publication No. 63-272349). These methods, however, require to add an additive in order to prevent the water-absorbing resin from deteriorating. From the point of view of safety, it is not preferable to add another additives, considering that the water-absorbing resin is to be used in sanitary materials or the like.

In this connection, a greater amount of cross-linking agent may be used to increase a cross-linking density of the water-absorbing resin so that the strength of the gel is enhanced and therefore the durability is improved. However, if a greater amount of cross-linking agent that is sufficient for the water-absorbing resin to have enough durability is used, the absorbency decreases significantly. As such, currently, water-absorbing resin that is excellent in safety, high in absorbency, and excellent in durability has not been realized, yet.

Further, in the case where the water-absorbing resin is used in, for example, diapers, there arise additional problems of stickiness of the swelled gel and reduction in the liquid permeability, in addition to the problem of durability mentioned above. The water-absorbing resin contains a water-soluble portion (the portion will be referred to as a water-soluble content). Because of the

presence of the water-soluble content, the swelled gel having absorbed water may become sticky. Further, in the case where the water-absorbing resin is used in absorbing products such as diapers, the liquid permeability may be reduced due to the stickiness. Therefore, when additional urine is supplied, the urine may be leaked. Normally, the amount of water-soluble content and the absorbency are in positive correlation. In order to reduce the water-soluble content, the cross-linking density of the water-absorbing resin needs to be increased. Therefore, if the water-absorbing resin has less water-soluble content, the absorbency also becomes lower.

However, it has been publicly known that the more proportion of the cross-linking agent in the water-absorbing resin is, the more improved the durability would be. However, there is a problem in that the absorbency decreases as the amount of cross-linking agent increases. Further, there has been disclosed a technique in which a chain transfer agent is used in production of water-absorbing resins to improve the absorbency (USP4698404). In this case, however, only few increase in the absorbency is observed for human urine, while the absorbency assuredly improves for water and physiological saline.

[Problem to be solved by the invention]

The present invention is in view of the current

situation described above, and has as an object to provide a production method of a water-absorbing resin excellent in durability.

Another object of the present invention is to provide a production method of a water-absorbing resin that (i) exhibits high absorbency with respect to a physiological saline and especially to a human urine, (ii) exhibits excellent durability when used in disposable diapers, (iii) prevents diapers from exuding liquid absorbed therein, (iv) can form a gel that is less sticky, and (v) exhibits excellent liquid permeability.

[Means for solving problem and effect]

In order to solve the above problems, the inventors have diligently researched, and finally found the followings:

(1) By performing aqueous polymerization, using a particular amount of cross-linking agent (B), on a water-soluble ethylene-based unsaturated monomer (A) aqueous solution that has a concentration in a particular range and contains water-soluble chain transfer agent (C), desirable water-absorbing resin (D) whose (i) durability has improved, (ii) can form gel that is less sticky, and (iii) liquid permeability has improved, while maintaining high absorbency, due to reduced molecular weight of the water-soluble content can be produced with good productivity.

(2) Further, by cross-linking, using hydrophilic cross-linking agent (E), the vicinity of the surface of the water-absorbing resin (D) produced by production method (1) described above, water-absorbing resin (F) that exhibits (a) better water absorbency, (b) better durability, (c) less gel stickiness, (d) better liquid permeability, and (e) better water absorption property, while maintaining high absorbency, can be produced.

In other words, the present invention relates to:

a production method of a water-absorbing resin (D) excellent in durability, which method is adapted so that the method includes performing aqueous polymerization using a monomer (A) aqueous solution that has a concentration in the range of from 30% by weight to a saturation concentration and contains (i) water-soluble ethylene-based unsaturated monomer (A), (ii) 0.005 mol% to 5 mol% of cross-linking agent (B) with respect to monomer (A), and (iii) 0.001 mol% to 1 mol% of water-soluble chain transfer agent (C) with respect to monomer (A); and

a production method of a water-absorbing resin (D) excellent in durability, which method is adapted so that the method includes performing cross-linking in the vicinity of a surface of water-absorbing resin (D) is cross-linked by a hydrophilic cross-linking agent that is reactive with a functional group contained in

water-absorbing resin (D), which water-absorbing resin (D) is produced by aqueous polymerization performed using a monomer (A) aqueous solution that has a concentration in the range of from 30% by weight to a saturation concentration and contains (i) water-soluble ethylene-based unsaturated monomer (A), (ii) 0.005 mol% to 5 mol% of cross-linking agent (B) with respect to and monomer (A), and (iii) 0.001 mol% to 1 mol% of water-soluble chain transfer agent (C) with respect to monomer (A).

The following specifically describes the present invention.

Water-soluble ethylene-based unsaturated monomer (A) (the monomer will be referred to as monomer (A)) of the present invention contains a functional group. Examples of monomer (A) include acrylic acid, methacrylic acid, maleic acid, fumaric acid, crotonic acid, itaconic acid, vinylbenzenesulfonic acid, 2-(meth)acrylamide-2-methylpropanesulfonic acid, 2-(meth)acryloylethanesulfonic acid, 2-(meth)acryloylpropanesulfonic acid, and their alkali metal salts and ammonium salts; and acrylamide, methacrylamide, 2-hydroxyethyl(meth)acrylate, methoxypolyethyleneglycol(meth)acrylate, N,N-dimethylaminoethyl(meth)acrylate, N,N-diethylaminopropyl(meth)acrylate,

N,N-diethylaminopropyl(meth)acrylamide, and their quaternary salts. At least one of the above may be selected and used.

In view of properties and costs of water-absorbing resin that is produced, it is preferable that acrylic acid, among monomers (A) listed above, be used as a main content. In this case, acrylic acid and its alkali metal salt and/or ammonium salt is contained, preferably, at a percentage of 50% by weight or greater, and more preferably, at a percentage of 75% by weight or greater with respect to monomer (A).

Further, in order to produce a water-absorbing resin excellent in durability, in the present invention, it is necessary to use a particular amount of cross-linking agent (B) that contains two or more polymerizable unsaturated groups and/or a reactive functional group per molecule. As cross-linking agent (B), for example a compound containing two or more polymerizable unsaturated group per molecule may be used. Examples thereof include N,N'-methylenebisacrylamide, (poly)ethyleneglycoldi(meth)acrylate, (poly)propyleneglycoldi(meth)acrylate, glycerictri(meth)acrylate, glycericacrylatemethacrylate, multivalent metal salts of (meth)acrylic acid, trimethylolpropanetri(meth)acrylate, triallylamine, triallylcyanurate, triallylisocyanurate, and

triallylphosphate and the like. Further, examples of cross-linking agent (B) containing reactive functional groups in the case where monomer (A) contains a carboxyl group include: polyhydric alcohols such as ethylene glycol; diethylene glycol, triethylene glycol, polyethyleneglycol, propylene glycol, dipropylene glycol, polypropylene glycol, and glycerin; multivalent glycidyl compounds such as (poly)ethylene glycoldiglycidylether, and glycerolpolyglycidylether; multivalent amines such as ethylenediamine, and polyethyleneimine; multivalent isocyanate compounds; multivalent metal salts and the like. Further, examples of cross-linking agent (B) containing both a polymerizable unsaturated group and a reactive functional group per molecule include glycidyl(meth)acrylate and N-methylol(meth)acrylamide. From the points of view of durability and water absorbency of the water-absorbing resin that is produced, it is especially preferable to use at least one of the compounds containing more than one polymerizable unsaturated groups in a molecular, among the cross-linking agents (B).

The amount of cross-linking agent (B) to be used in the present invention is 2 to 10 times greater in mol, or more preferably 4 to 10 times greater in mol than the amount of the cross-linking agent used in the case where the polymerization is performed under the same

conditions, except that water-soluble chain transfer agent (C) is not used to obtain a target water-absorbency. Specifically, the amount of cross-linking agent (B) to be used is 0.005 mol% to 5 mol% with respect to monomer (A). If less than 0.005 mol% of cross-linking agent (B) is used, a water-absorbing resin with high absorbency is produced. However, the water-absorbing resin is inferior in durability, contains many water-soluble contents, and has a higher molecular weight. This causes the gel of the water-absorbing resin to be stickier, and the liquid permeability to be degraded. On the other hand, if more than 5 mol% of cross-linking agent (B) is used, the absorbency becomes extremely low. Further, it is preferable that the amount of cross-linking agent to be used be in the range of from 0.02 mol% to 1 mol%, more preferably in the range of from 0.04 mol% to 0.4 mol%, and even more preferably in the range of from 0.08 mol% to 0.2 mol%, although it depends upon the amount of water-soluble chain transfer agent (C) to be used. The amount of water-soluble chain transfer agent (C) will be described later.

Further, in addition to the above method utilizing cross-linking agent (B), a method in which graft polymerization is performed to form a cross-link may be carried out simultaneously. For example, the monomer (A) aqueous solution may be polymerized in the presence of a

hydrophilic polymer (e.g., cellulose, starch, polyvinyl alcohol), so that a cross-link is formed as a result of the graft polymerization. It is preferable that the water-soluble macromolecule be used in the range of from 1% by weight to 50% by weight with respect to monomer (A).

In the present invention, it is necessary to use a particular amount of water-soluble chain transfer agent (C).

According to the present invention, (i) a particular amount of water-soluble chain transfer agent (C) is selected, and (ii) a large amount of cross-linking agent is used in polymerization to form a high cross-link, which amount is 2 to 100 greater in mol than that used in an ordinary production method. With such an arrangement, the present invention provides an excellent water-absorbing resin that (i) is highly excellent in durability, (ii) exhibits high absorbency not only to physiological saline but also to human urine, (iii) provides less negative influence (e.g., stickiness of gel, decrease in the liquid permeability) due to low molecular weight of the water-soluble content can be produced.

The water-soluble chain transfer agent (C) for use in the present invention is not particularly limited, provided that water-soluble chain transfer agent (C) is soluble in water or in a water-soluble ethylene-based unsaturated

monomer. The water-soluble chain transfer agent (C) may be a thiol, a thiol acid, a secondary alcohol, an amine, a hypophosphite, or the like. Specific examples of the water-soluble chain transfer agent (C) include: mercaptoethanol, mercaptopropanol, dodecyl mercaptan, thioglycolic acid, thiomalic acid, 3-mercaptopropionic acid, isopropanol, sodium hypophosphite, formic acid, and their salts. One of, or two or more of the water-soluble chain transfer agents (C) are selected and used. Because of their effect, it is preferable that the water-soluble chain transfer agent (C) be hypophosphite such as sodium hypophosphite.

An amount of the water-soluble transfer agent (C) to add is, with respect to monomer (A), in the range of from 0.001 mol% to 1 mol%, preferably in the range of from 0.005 mol% to 0.3 mol%, even though it depends on the type and amount of internal cross-linking agent (B) and the concentration of monomer (A) aqueous solution. In the case where the amount is less than 0.001 mol%, the amount of cross-linking agent (B) to be used in the present invention is not preferable because the cross-linking density would become high and the absorbency would become too low. Further, it is not preferable to use more than 1 mol% of cross-linking agent (B) because the water-soluble content would increase and the durability would decrease.

The concentration of monomer (A) aqueous solution used in the present invention is in the range of from 30% by weight to the saturation concentration. It is more preferable that the concentration be in the range of from 35% by weight to the saturation concentration. If the concentration is below 30% by weight, the productivity per unit-reaction-volume decreases. Moreover, the drying step takes longer time, and therefore the productivity decreases. Therefore, from industrial view, the concentration below 30% by weight is not preferable. In conventional polymerization methods, if the polymerization is performed at a concentration close to the saturation concentration in order to improve the productivity, unnecessary reactions such as self-cross-linking occur, and the absorbency is decreased. Therefore, the amount of cross-linking agent (B) that can be used in the polymerization is limited, and thus only a water-absorbing resin having poor durability is produced. However, with the method of the present invention, self-cross-linking reaction is prevented by choosing the amount of water-soluble chain transfer agent (C) to be used. This makes it possible to increase the amount of cross-linking agent (B) to be used, and therefore a water-absorbing resin that is excellent in durability and has high absorbency can be produced at a high concentration at good productivity.

Further, if necessary, a thickener may be used in the monomer (A) aqueous solution. Examples of the thickener include: polyvinylpyrrolidone; polyacrylamide; methyl cellulose; and hydroxyethyl cellulose and the like.

In the present invention, among publicly-known polymerization techniques (e.g., aqueous polymerization, reverse-phased suspension polymerization, precipitate polymerization, bulk polymerization, polymerization by activation energy such as ultraviolet ray or electron ray), aqueous polymerization is employed for polymerizing using the monomer (A) aqueous solution to produce a water-absorbing resin that has excellent properties and productivity, and requires less costs. Exemplary methods of aqueous polymerization include: casting polymerization performed in a cast (Japanese Examined Patent Publication No. 48-42466 (Tokukosho 48-42466)); polymerization performed using a belt conveyer (Japanese Unexamined Patent Publication No. 58-49714 (Tokukaisho 58-49714)); and polymerization performed in, for example, a kneader having a stir blade that can comminute hydrate gel polymers (Japanese Unexamined Patent Publication No. 57-34101 (Tokukaisho 57-34101)).

In performing the aqueous polymerization, it is preferable that (i) chain transfer reaction take place uniformly with water-soluble chain transfer agent (C) and (ii) the cross-linking reaction occurs uniformly with

cross-linking agent (B). In order to produce a water-absorbing resin having better properties, it is preferable that the heat generated during the polymerization be removed uniformly. In order to do so, it is preferable that, instead of the polymerization method in which the polymerized gel is kept as one united body, the polymerized gel of the reaction system be stirred from the beginning to the end of the polymerization, or sometimes during the polymerization or throughout the polymerization so that the heat generated during the polymerization be removed uniformly, instead of a polymerization method in which the polymerized gel is unified. It is thus preferable that the polymerization reaction be performed in a reactor vessel having a rotation stir blade. The reactor vessel having a rotation stir blade is not particularly limited, but a reactor vessel that can stir the polymerized gel with greater power is preferable. An exemplary reactor vessel is a vessel that shears the polymerized gel by the rotation stir blade, which polymerized gel is generated as the polymerization proceeds. Further, in order to increase the stirring power, it is preferable that a plurality of rotation stir blades be provided. Examples of the reactor vessel include a single-screwed mix-kneader, a single-screwed extruder, a two-screwed kneader, and a three-screwed kneader. Further, by using the two-screwed kneader, polymerized

gel can be fragmented and stirred evenly throughout the polymerization, and the heat generated during the polymerization can be removed uniformly. As a result, a water-absorbing resin having excellent properties can be produced. Therefore, it is preferable to use a two-screwed kneader.

In the present invention, the radical polymerization initiator to be used in the aqueous polymerization is not particularly limited, as long as the radical polymerization initiator is water-soluble. For example, the followings may be used as the radical polymerization initiator: persulfates such as potassium persulfate, ammonium persulfate, sodium persulfate and the like; hydroperoxides such as hydrogen peroxide, t-butylhydroperoxide, cumenehydroperoxide and the like; azo compounds such as 2,2'-azobis(2-amizino propane)dihydrochloride) and the like; secondary cerium salt, permanganate, and the like. In view of, for example, (i) properties of the water-absorbing resin to be produced and (ii) safety of decomposition products, it is preferable that the radical polymerization initiator be one or more of persulfate, hydroperoxide, and azo compounds.

Further, in the case where the radical polymerization initiator is an oxidizing radical polymerization initiator, reductants may be combined to be used as a redox type initiator. Examples of the reductants include: sulfites

(hydrogen salt) such as sodium sulfite, sodium hydrogen sulfite and the like; thisulfate such as sodium thiosulfate and the like; dithionite; metal salt such as copper sulfate, iron sulfate and the like; organic reductants such as b-ascorbic acid and the like; aniline; and amines such as monoethanolamine and the like.

Although a wide range of the amount of the radical polymerization initiator may be used, normally it is preferable that the range of the amount of the radical polymerization initiator be 0.001 mol% to 2 mol% with respect to monomer (A), or more preferably 0.01 mol% to 0.5 mol% with respect to monomer (A). If less than 0.001 mol% of radical polymerization initiator is used, the induction period becomes longer and the amount of the residual monomer easily increases. Further, in a conventional polymerization method, if the amount of the polymerization initiator is increased in order to (a) reduce the amount of the residual monomers or (b) shorten the induction period and the polymerization period, unnecessary reactions such as self-cross-linking may occur, thereby degrading the absorbency. Thus, the amount of initiator has been limited. On the contrary, with the present invention, these disadvantages are solved, and the water-absorbing resin having excellent properties is produced even when the amount of initiator is increased. If, however, more than 2 mol% of radical polymerization

initiator is used, not only expected effects from the increased amount cannot be achieved, but also it becomes difficult to control the polymerization reaction. Accordingly, it is not preferable to use more than 2 mol% of radical polymerization initiator.

The water-absorbing resin produced by the present invention may be polymerized at high concentration, and the water-absorbing resin may be dried with the heat generated during the polymerization while being polymerized. Depending upon the proportion of water contained after performance of the polymerization, the hydrate gel produced may be dried further and then used in the water-absorbing resin. For the drying, publicly-known drying methods may be employed. Exemplary methods thereof include: azeotropy dehydration in an organic solvent; drying with a mechanical draft oven; drying with a reduced-pressure dryer; drying with a microwave dryer; drying with an infrared dryer; and drying with a belt having heated to a predetermined temperature or a drum dryer having heated to a predetermined temperature. It is preferable that the polymerized hydrate gel be dried by one of the above methods at 80°C or above. It is more preferable that the hydrate gel be dried at 80°C to 230°C. In view of productivity, it is not preferable to dry the hydrate gel at a temperature below 80°C because it consumes too much

time. Careful attention is required in drying the hydrate gel at 230°C or above because the water-absorbing resin may be deteriorated at such high temperature.

Further, the water-absorbing resin produced by the polymerization and the drying is pulverized and/or classified, if necessary, before being used.

Further, the present invention also provides a production method of water-absorbing resin (F). In the production method, the water-absorbing resin (F) is produced by cross-linking, with particular hydrophilic cross-linking agent (E), in the vicinity of the surface of water-absorbing resin (D) produced by the production method described above. Water-absorbing resin (D) produced by the production method of the present invention has significantly improved water absorbency, compared with conventional water-absorbing resins. Further, water-absorbing resin (F), on which cross-linking was performed in the vicinity of the surface, has better durability and water absorbency than water-absorbing resin (D), on which cross-linking has not been performed in the vicinity of the surface.

Hydrophilic cross-linking agent (E) used in the present invention is compound (E-1) containing more than one functional group per molecule and/or multivalent metal salt (E-2) containing more than one functional group per molecule, which functional group is reactive

with a carboxyl group. Examples of compounds (E-1) in the case where water-absorbing resin (D) contains a carboxyl group include: polyhydroxy alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethyleneglycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentylglycol, propylene glycol, glycerin, polyglycerin, trimethylolpropane, pentaerythritol, sorbitol, polyvinyl alcohol and the like; ethylene glycoldiglycidylether; multivalent glycidylether compounds such as ethyleneglycoldiglycidylether, polyethyleneglycoldiglycidylether, glycerolpolyglycidylether, diglycerolpolyglycidylether, polyglycerolpolyglycidylether, propylene glycoldiglycidylether, polypropylene glycoldiglycidylether and the like; multivalent amine compounds such as ethylenediamine, diethylenetriamine, triethylenetetramine, polyethyleneimine and the like; multivalent oxazoline compounds such as 1,2-ethylenebisoxazoline, polyisopropenyloxazoline and the like; haloepoxy compounds such as epichlorohydrin and the like; multivalent aziridine compounds; and multivalent isocyanate compounds; and the like. Examples of multivalent metal salt (E-2) in the case where water-absorbing resin (D) contains a carboxyl group include: hydroxide of zinc, hydroxide of calcium, hydroxide of magnesium, hydroxide of aluminum,

hydroxide of iron, hydroxide of zirconium, chloride of zinc, chloride of calcium, chloride of magnesium, chloride of aluminum, chloride of iron, and chloride of zirconium, and the like. It is preferable that one kind or more than one kind of the above be used. It is preferable to use compound (E-1) as an essential component. In view of surface cross-linking effects, it is especially preferable that a polyhydric alcohol, a multivalent glycidyl compound, or a multivalent amine be used as hydrophilic cross-linking agent (E). Further, a combination of compound (E-1) and multivalent metal salt (E-2) may be used as hydrophilic cross-linking agent (E) to improve combined properties.

The amount of hydrophilic cross-linking agent (E) used in the present invention is 0.005 parts by weight to 5 parts by weight with respect to 100 parts by weight of water-absorbing resin (D) produced by the production method described above. It is preferable that the amount be in the range of from 0.01 parts by weight to 1 part by weight with respect to 100 parts by weight of water-absorbing resin (D) produced by the production method described above. If the amount is within this range, water-absorbing resin (F) having excellent properties and cross-linked surface can be produced. If more than 5 parts by weight of hydrophilic cross-linking agent (E) is used, it is not only uneconomical, but also

may cause unreacted hydrophilic cross-linking agent (E) to remain in water-absorbing resin (F) that has been produced. Moreover, this amount of hydrophilic cross-linking agent (E) is excess for achieving desired cross-linking effects, reducing the water absorbency of water-absorbing resin (F) that is produced. Therefore, it is not preferable to use more than 5 parts by weight of hydrophilic cross-linking agent (E). Further, in the case where less than 0.005 parts by weight of hydrophilic cross-linking agent (E) is used, it is difficult to achieve the effects of the present invention.

In the present invention, water and/or hydrophilic organic solvent (G) may be used in mixing water-absorbing resin (D) and hydrophilic cross-linking agent (E).

In the present invention, the amount of water to be used is 0 part to 20 parts by weight with respect to 100 parts by weight of water-absorbing resin (D). It is preferable that the amount be in the range of from 0.5 parts by weight to 10 parts by weight.

Examples of hydrophilic organic solvent (G) include: lower alcohols such as methanol, ethanol, n-propanol, iso-propanol, n-butanol, iso-butanol, t-butanol and the like; ketones such as acetone, methylethylketone, methylbutylketone and the like; ethers such as dioxane tetrahydrofuran and the like; amides such as N,N-dimethylformamide and the like; and sulfoxides such

as dimethylsulfoxide and the like. The amount of water-absorbing resin (D) to be used is in the range of from 0 parts by weight to 20 parts by weight with respect to 100 parts by weight of water-absorbing resin (D). It is preferable that the amount be in the range of from 0 parts by weight to 8 parts by weight.

The followings are exemplary methods, according to the present invention, of (i) mixing water-absorbing resin (D) and hydrophilic cross-linking agent (E) and (ii) cross-linking in the vicinity of the surface of the water-absorbing resin:

(i) Hydrophilic cross-linking agent (E) and, if necessary, a mixed solution of water (water vapor) and/or hydrophilic organic solvent (G) may be added to water-absorbing resin (D) by spraying or dropping;

(ii) Water-absorbing resin (D) is dispersed and suspended in a hydrophobic organic solvent that is inactive in polymerization, and hydrophilic cross-linking agent (E) and, if necessary, water and/or hydrophilic organic solvent (G) are added while being stirred; and

(iii) water-absorbing resin (D) is dispersed in a mixed solvent of water and hydrophilic organic solvent (G), and hydrophilic cross-linking agent (E) is added.

In case (ii), it is preferable that hydrophilic cross-linking agent (E) be emulsified, using a particular surfactant, into a hydrophobic organic solvent and be

suspended in advance, and then the emulsified solution be added to a solution in which water-absorbing resin (D) has been dispersed and suspended.

As described above, an ordinary heating machine or heating oven may be used to perform a heating treatment on a mixture of (i) water-absorbing resin (D) produced by the method of the present invention, (ii) hydrophilic cross-linking agent (E), and, if necessary, water and/or hydrophilic organic solvent (G). Examples of the heating machine and the heating oven include: a trench type mixing dryer; a rotary type dryer; a disk type dryer; a kneading dryer; a fluidized bed type dryer; an air-flow type dryer; an infrared dryer; a dielectric heating dryer; and the like. Further, hydrophilic cross-linking agent (E) may be added, in an organic solvent, to water-absorbing resin (D) by method (ii), and thereafter heated to react in the organic solvent.

It is preferable that the heat treatment be performed at the heating treatment in the range of from 40°C to 250°C, more preferably in the range of from 90°C to 220°C, although it depends upon which kind of hydrophilic cross-linking agent (E) is used. If the heating treatment is performed at a temperature below 40°C, not only it takes time to react and therefore the productivity decreases, but also a part of hydrophilic cross-linking agent (E) may not react and may remain in water-absorbing resin (F) that is

produced. Therefore, it is not preferable that the heating treatment be performed at a temperature below 40°C. On the other hand, if the heating treatment is performed at a temperature above 250°C, deterioration by the heat may occur in some kinds of water-absorbing resin (D). Therefore, careful attention is required.

Note that water-absorbing resin (F) whose surface is cross-linked or water-absorbing resin (D) whose surface is not cross-linked may be pulverized and agglomerated, if necessary.

[Effect of the invention]

The water-absorbing resin produced by the method of the present invention has the following advantages, which could not be achieved by the conventional methods: excellent durability of swelled gel; high absorbency with respect to physiological saline and especially to human urine; low molecular weight of the water-soluble content; significantly reduced stickiness of swelled gel; significantly improved liquid permeability; and excellent safety. According to the method of the present invention, such excellent water-absorbing resin can be easily produced by performing aqueous polymerization, in the presence of a particular amount of cross-linking agent (B) and a particular amount of water-soluble chain transfer agent (C), on water-soluble ethylene-based unsaturated monomer (A). Furthermore, by cross-linking, using

particular hydrophilic cross-linking agent (E), in the vicinity of the surface of water-absorbing resin (D) that has been produced, water-absorbing resin (F) having significantly improved absorption rate and durability can be produced. Water-absorbing resin (D) and water-absorbing resin (F) that have excellent water absorbency can be produced inexpensively. This could not be achieved by a conventional water-absorbing resin. Therefore, water-absorbing resin (D) and water-absorbing resin (F) may be widely used in various fields including sanitary material, foods, civil engineering, agriculture.

As described above, the water-absorbing resin produced by the production method of the present invention has the following advantages.

(1) The swelled gel has excellent durability because, in the present invention, the high absorbency is maintained even when a large amount of cross-linking agent is used. In contrast, conventional swelled gels have had poor durability because polymerization is performed using a reduced amount of cross-linking agent in order to produce a water-absorbing resin having high absorbency.

(2) The absorbency with respect to human urine is high. This could not be achieved by the conventional water-absorbing resins.

(3) The water-absorbing resins can be produced at high productivity because even when the monomer is

polymerized at a high concentration close to the saturation concentration, a water-absorbing resin having excellent properties can be produced without causing unnecessary reactions such as self-cross-linking. Therefore, the polymerization can be performed at a high concentration.

(4) The water-absorbing resin of the present invention has high absorbency, and the water-soluble content associated therewith does not provide negative influences (e.g., stickiness of swelled gel due to water-soluble content, reduction in the liquid permeability) because the molecular weight of the water-soluble content is small.

(5) By performing the cross-linking in the vicinity of the surface, (i) the water absorbency can be better than the absorbency achieved by a conventional surface cross-linking of water-absorbing resin, and (ii) the durability and the absorption rate can be improved.

(6) A small amount of residual monomer is used, because high absorbency can be achieved even when an increased amount of polymerization initiator is used. In contrast, conventionally, if the amount of polymerization initiator is increased in order to reduce the residual monomer or shorten the induction period and polymerization period, unnecessary reaction such as self-cross-linking is generated. Therefore, high absorbency

could not be achieved.

(Examples)

The following describes the present invention, with reference to Examples. The scope of the present invention, however, is not limited to the Examples. Note that the properties of the water-absorbing resin in the Examples indicate the values measured by the testing methods described later. Further, the term "part(s)" means "part(s) by weight".

(1) Absorbency of physiological saline

In a beaker containing 150 ml of 0.9% by weight sodium chloride aqueous solution, 1.0 g of water-absorbing resin was soaked and stirred slowly using a magnetic stirrer. After six hours had passed, the swelled gel was filtered by a wire net, and the weight of the swelled gel from which water had been removed adequately was measured. Then, the absorbency was calculated using the formula below.

$$\text{absorbency(g/g)} = \frac{\text{weight of swelled gel}}{\text{weight of water-absorbing resin}}$$

(2) Absorbency of human urine

The absorbency of human urine was measured under the same conditions, except that sample human urine of 10 adult males were used instead of the physiological

saline used in the case (1).

(3) Water-soluble content

In 1000 ml of deionized water, 0.5 g of water-absorbing resin was dispersed. After 12 hours had passed, this was filtered by a paper filter, and the solid content in the filtrate was measured. Then, the water-soluble content was calculated using the formula below.

water-soluble content (%) =

$$\frac{\text{weight of filtrate (g)} \times \text{solid content in filtrate (\%)}}{0.5 \text{ g}}$$

(4) Molecular weight of water-soluble content

By using, as standard, various polysodium acrylic acids whose molecular weights had already been calculated, the molecular weight of the water-soluble content obtained in item (3) was worked out by using gel permeation chromatography.

(5) Tolerance of swelled gel

A commercially-available diaper for children (weight: 72 g) formed of nonwoven fabric, cotton-like pulp, water-absorbing paper, and water-proof film is cut into a half, and 2.5 g of polymer was evenly dispersed between the cotton-like pulp and the water-absorbing paper, and 120 ml of adult human urine was added. Then, the diaper

was left at 37°C. Thereafter, the diaper was opened to observe the state of the swelled gel after (i) 6 hours, (ii) 12 hours, and (iii) 18 hours. The degree of deterioration was evaluated using three categories: good, average, and poor.

Good : shape of swelled gel is maintained
Average : shape of swelled gel is partially collapsed
Poor : shape of swelled gel is collapsed,
and the swelled gel is muddy

(6) Amount of exudation of absorbed liquid

On the nonwoven fabric of the diapers for children after 18 hours, which diapers had been used in the examination of durability of the swelled gel, 10 sheets of 23-by-23-cm paper towels folded into two were overlaid. Then, a pressure of 40 g/cm² was applied for one minute. Thereafter, the amount of urine returned to the paper towels was measured.

(7) Stickiness of swelled gel

The stickiness (feeling of dryness) of the swelled gel whose absorbency had been calculated in (1) was determined by hand-touching. The feeling of dryness was evaluated using three categories: good, average, and poor.

Good : swelled gel is very dry,
providing feeling of dryness

Average : swelled gel is partially sticky

Poor : swelled gel is sticky,
and hand becomes slimy

(8) Liquid permeability of swelled gel

As illustrated in Figure 1, in a plate 1 having an inner diameter of 53 mm, 1.0 g of water-absorbing resin was placed and 10 ml of human urine was poured therein, thereby obtaining swelled gel 2. On the swelled gel 2, a paper towel 3 having a diameter of 53 mm was placed. Further, a test tube 4 made of acrylic resin, provided with a protruding cylinder, and having doughnut-shaped was placed at the center thereof, as illustrated in Figure 1. After this was left at a room temperature for one hour, 6 ml of human urine was poured from the inlet opening 5. The time taken for all of the human urine to be absorbed into the polymer was measured. The measured time is used as a parameter of the liquid permeability of the swelled gel.

(Example 1)

A monomer aqueous solution with the concentration of 37% and the neutralization ratio of 75% was produced using (i) 4380 g of 37% by weight aqueous solution containing 414 g of acrylic acid and sodium acrylic acid, (ii) 6.815 g (0.1 mol% with respect to monomer (A)) of trimethylolpropanetriacrylate, which functions as

cross-linking agent (B), (iii) 0.195 g (0.008 mol% with respect to monomer (A)) of sodium hypophosphite hydrate, which functions as water-soluble chain transfer agent (C), and (iv) 670 g of ion-exchange water. Thereafter, nitrogen gas was blown to expel dissolved oxygen.

In a reactor vessel having a lid and a twin-arm type kneader (content volume of 10 liters) made of stainless-steel and having a jacket and two sigma blades, a monomer (A) aqueous solution was supplied and nitrogen gas was blown to fill a reaction system with nitrogen. Thereafter, the two sigma blades were rotated, while hot water of 35°C was streamed in the jacket to heat, 2.62 g of ammonium persulfate and 0.12 g of sodium hydrogen sulfite, both of which function as polymerization initiators, were added to start polymerization. At a peak of polymerization, hydrate gel polymer was fragmented to have a diameter of approximately 5 mm. Then, the stirring was continued, and 60 minutes after the beginning of the polymerization, the lid was moved to take out the gel. The fine particles of hydrate gel polymer that had been produced were (i) dispersed over a wire net having 50 meshes and (ii) dried with hot air of 170°C for 50 minutes. Then, the dried hydrate gel polymer was pulverized with a hammer type pulverizer, and filtered by a wire metal having 20 meshes. As a result, water-absorbing resin (1) that had filtered through the wire net having 20 meshes

was produced.

The properties of water-absorbing resin (1) were evaluated, and results of the evaluation are shown in Table 1.

(Example 2)

The same operations as in Example 1 were performed, except that 1.219 g (0.05 mol% with respect to monomer (A)) of water-soluble chain transfer agent (C) sodium hypophosphitelhydrate was used. As a result, water-absorbing resin (2) was produced.

The properties of water-absorbing resin (2) were evaluated, and results of the evaluation are shown in Table 1.

(Example 3)

The same operations as in Example 1 were performed, except that (i) 21.988 g (0.2 mol% with respect to monomer) of polyethyleneglycoldiacrylate (n=8) was used as cross-linking agent (B), and (ii) 2.44 g (0.1 mol% with respect to monomer (A)) of water-soluble chain transfer agent (C) sodium hypophosphitelhydrate was used. As a result, water-absorbing resin (3) was produced.

The properties of water-absorbing resin (3) were evaluated, and results of the evaluation are shown in Table 1.

(Example 4)

The same operations as in Example 1 were performed,

except that (i) 54.97 g (0.5 mol% with respect to monomer) of cross-linking agent (B) polyethyleneglycoldiacrylate($n=8$) was used, and (ii) 9.76 g (0.4 mol% with respect to monomer (A)) of water-soluble chain transfer agent (C) sodium hypophosphite hydrate was used. As a result, water-absorbing resin (4) was produced.

The properties of water-absorbing resin (4) were evaluated, and results of the evaluation are shown in Table 1.

(Example 5)

The same operations as in Example 1 were performed, except that (i) 2.152 g of N,N'-methylenebisacrylamide (0.06 mol% with respect to monomer (A)) was used in place of cross-linking agent (B), and (ii) 3.45 g of thiomalic acid (0.1 mol% with respect to monomer) was used in place of water-soluble chain transfer agent (C). As a result, water-absorbing resin (5) was produced.

The properties of water-absorbing resin (5) were evaluated, and results of the evaluation are shown in Table 1.

(Example 6)

The same operations as in Example 1 were performed, except that (i) the amount of ion-exchange water to be used was changed to 50 g, (ii) the monomer (A) aqueous solution with the concentration of 42% was used, (iii) 17.07 g (0.1 mol% with respect to monomer (A)) of

polyethyleneglycoldiacrylate($n=14$) was used as cross-linking agent (B), and (iv) 0.69 g (0.02 mol% with respect to monomer (A)) of water-soluble chain transfer agent (C) thiomalic acid was used. As a result, water-absorbing resin (6) was produced.

The properties of water-absorbing resin (6) were evaluated, and results of the evaluation are shown in Table 1.

(Example 7)

Forty grams of corn starch and 600 g of ion-exchange water were placed in a reactor vessel provided with a stir-stick, a nitrogen gas blow tube, and a thermometer, stirred for one hour at 55°C, and thereafter cooled down to 30°C. To the starch aqueous solution, (i) 300 g of acrylic acid, (ii) 1.92 g (0.3 mol% with respect to monomer (A)) of N,N'-methylenebisacrylamide, which functions as cross-linking agent (B), (iii) 0.94 g (0.15 mol% with respect to monomer (A)) of thiomalic acid, which functions as water-soluble chain transfer agent (C), were solved.

As a result, a monomer aqueous solution with the concentration of 33% and the neutralization ratio of 0% was produced.

The monomer aqueous solution was adjusted to 35°C, and 0.20 g of sodium persulfate, which functions as the polymerization initiator, and 0.04 g of l-ascorbic acid were added and then stirred for three hours to be polymerized.

To a hydrate gel polymer, 389 g of 30% by weight caustic soda aqueous solution was added so that the neutralization ratio is adjusted to 70%. Then, it was dried and pulverized in the same manner as in Example 1. As a result, water-absorbing resin (7) was produced.

The properties of water-absorbing resin (7) were evaluated, and results of the evaluation are shown in Table 1.

(Example 8)

To 72 g of acrylic acid, 22.2 g of deionized water was added. A mixture produced thereby was used as a neutralizer, and (i) 49.5 g of potassium hydroxide with the purity of 85%, (ii) 0.1 g (0.065 mol% with respect to monomer (A)) of N,N'-methylenebisacrylamide, which functions as cross-linking agent (B), 0.225 g (0.15 mol% with respect to monomer (A)) of thiomalic acid, which functions as water-soluble chain transfer agent (C), were added sequentially. As a result, a monomer aqueous solution with the concentration of 70% and the neutralization ratio of 75% was produced.

This monomer aqueous solution was kept at 70°C in a nitrogen air stream with a thickness of approximately 5 mm. Then, 0.1 g of ammonium persulfate and 0.02 g of sodium hydrogen sulfite were added, and polymerization was performed. The polymerization started immediately. After 10 minutes had passed, a polymerized gel that was

almost dried was taken out, dried, and pulverized, in the same manner as in Example 1. As a result, water-absorbing resin (8) was produced.

The properties of water-absorbing resin (8) were evaluated, and results of the evaluation are shown in Table 1.

(Example 9)

To 100 parts of water-absorbing resin (5) that had been produced in Example 1, 0.1 part of ethylene glycoldiglycidylether, five parts of water, and one part of isopropyl alcohol were added. Thereafter, a mixture produced thereby was treated, in a dryer, with heat at 100°C for 30 minutes. As a result, water-absorbing resin (9) was produced.

Water-absorbing resin (9) that had been produced in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Example 10)

To 100 parts of water-absorbing resin (2) that had been produced in Example 2, one part of glycerin, six parts of water, and one part of acetone were added. Thereafter, the mixture was (i) putted into a blender whose jacket had been heated to 230°C by a heating medium, (ii) mixed, and (ii) treated with heat. As a result, water-absorbing resin (10) was produced.

Water-absorbing resin (10) that had been produced

in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Example 11)

To 100 parts of water-absorbing resin (3) that had been produced in Example 3, a solution composed of (i) 0.1 parts of ethyleneglycidylether, 3 parts of water, and 6 parts of methanol were added. A mixture produced thereby was treated, in a dryer, with heat at 130°C for one hour. As a result, water-absorbing resin (12) was produced.

Water-absorbing resin (11) that had been produced in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Example 12)

To 100 parts of water-absorbing resin (4) that had been produced in Example 4, 10 parts of aqueous solution composed of (i) one part of aluminium sulfate, (ii) one part of glycerin, and (iii) 8 parts of water were added. A mixture produced thereby was treated with heat at 200°C for 30 minutes. As a result, water-absorbing resin (12) was produced.

Water-absorbing resin (12) that had been produced in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Comparative Example 1)

The same operations as in Example 7 were performed, except that 0.273 g of cross-linking agent (B) (0.004 mol%

with respect to monomer (A)) was used. As a result, comparative water-absorbing resin (1) was produced.

Comparative water-absorbing resin (1) that had been produced in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Comparative Example 2)

The same operations as in Example 7 were performed, except that water-soluble chain transfer agent (C) sodium hypophosphitelhydrate was not added. As a result, comparative water-absorbing resin (2) was produced.

Comparative water-absorbing resin (2) that had been produced in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Comparative Example 3)

The same operations as in Example 1 were performed, except that (i) water-soluble chain transfer agent (C) sodium hypophosphitelhydrate was not added and (ii) 3.41 g of cross-linking agent (B) (0.05 mol% with respect to monomer (A)) was used. As a result, comparative water-absorbing resin (3) was produced.

Comparative water-absorbing resin (3) that had been produced in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Comparative Example 4)

The same operations as in Example 1 were performed, except that (i) water-soluble chain transfer agent (C)

sodium hypophosphite hydrate was not added and (ii) cross-linking agent (B) was replaced by 17.73 g of N,N'-methylenebisacrylamide (0.5 mol% with respect to monomer (A)). As a result, comparative water-absorbing resin (4) was produced.

Comparative water-absorbing resin (4) that had been produced in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Comparative Example 5)

The same operations as in Example 7 were performed, except that cross-linking agent (B) was not added. As a result, comparative water-absorbing resin (5) was produced.

Comparative water-absorbing resin (5) that had been produced in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Comparative Examples 6 to 8)

The same operations as in Example 9 were performed using comparative water-absorbing resins (1) to (3) that had been produced in Comparative Examples 1 to 3, respectively. As a result, comparative water-absorbing resins (6) to (8) were produced.

Comparative water-absorbing resins (6) to (8) that had been produced in the manner described above were analyzed, and results of the analysis are shown in Table 1.

4. Brief description of drawings

Figure 1 illustrates a test equipment for testing the liquid permeability of a swelled gel.

1 plate

2 swelled gel

3 paper towel

4 test vessel made of acrylic resin

5 inlet opening

Applicant NIPPON SHOKUBAI KAGAKU KOGYO Co., Ltd.

Table 1

[illegible]

Comp. example	Comp. W.A.R	TMPT	0.004	SHP	0.008	85	8	P	35.5	93	60or more	P/P/P	18.3
(1)	(1)												
(2)	(2)	TMPT	0.1	NONE	0	36	21	G	5.2	9	50	G/G/G	13.5
(3)	(3)	TMPT	0.05	NONE	0	43	20	A-G	6.2	8	60	G/G/A-G	18.3
(4)	(4)	MBAA	0.5	NONE	0	25	18	G	3	1	40	P/P/P	22.5
(5)	(5)	NONE	0	thiomalic acid	0.1	85	11	P	45.2	100	60or	G/A/G-P	16.3
(6)	(6)					55	19	A	33.1	90	more	A/A-P/P	11.3
(7)	(7)					34	24	G	5	8	60	G/G/A-G	13.1
(8)	(8)	(surface treated example 1)				39	21	G	5.2	8	30	(G:good A:average P:poor)	15.1
		(↑			comparative example 2)								
		(↑			comparative example 3)								

MBAA : N,N'-methylenebisacrylamide

TMPT : trimethylolpropanetriacrylate

PEGDA : polyethyleneglycoldiacrylate (n=8 or 14)

SHP : sodium hypophosphite hydrate

(A) 水溶液を混合させ、混合時にグラフト重合に起因する吸熱を形成させる方法が挙げられ、これらの水溶性高分子は増量体 (A) に対して 1~50 重量%の範囲で用いるのが好ましい。

本発明は特定量の水溶性遷移動剤(C)を用いることが必須である。

[illegible]

本発明に使用する水溶性型顔料動機(C)としては、水または水溶性エチレン性不飽和單體に溶解するものであれば特に制限されず、チオール類、チオール健康、2級アルコール類、アミン類、

5 重量% 炭酸塩度の範囲である。3.0 重量% 炭酸塩度の範囲では単位反応投量当りの生産性が下がり、また乾燥工程にも時間を要し、生産性が低下して工費的観点から好ましくない。従来の重合方法では生産性向上のため飽和濃度付近で重合を行つと自己凝結などの不要な反応が起り吸水倍率が低下するため、重合時に使用できる乾燥剤(B)の量が限られ、そのため耐久性に乏しい吸水性能の膜が得られなかった。しかし本発明の方法によれば、水溶性塩類移動剤(C)の使用量を上述のことによって自己凝結反応が抑制され、乾燥剤(B)の使用量が増やせるので耐久性に優れた高吸水塩類の吸水性能膜を高濃度で生産性よく製造することが出来る。

また必要に応じて草履体(A)水溶液に増粘剤を用いてもよい。この様な増粘剤としては、例えばポリビニルピロリドン、ポリアクリルアミド、メチルセルロース、ヒドロキシエチルセルロース等を挙げることが出来る。

本発明に於て単體は(A)水溶液を配合せしめ取水

均一な除去がなされることが好ましく、よって、
合反応は回転様質を有する反応容器で行われ
ることが好ましい。回転様質を有する反応容器
としては、特に耐腐はしないが、重合ゲルに対する
抵抗力が大きいものが好ましく、重合の進行に準
び生成する重合ゲルを回転様質によって剪断力が大
きくするものでも可示でも、また抵抗力が大
きくするために回転様質は複数であることが望
ましい。反応槽としては例えば一軸の連続
攪、一軸の押出機、双軸型、二軸型、三軸二
軸型などが挙げられる。また双回転ローダーを
用いると、重合ゲルを細かく細分化し重合の全時
間にならわたり均一に原料がでも重合熱の均一な除去
を行えるので、より性能の優れた吸水樹脂が得
られるので好ましい。

本説明書に対して、水溶性配合に使用されるラジカル重合開始剤としては水溶性であり特に制限はありません。例えば過硫酸カリウム、過酸化アンモニウム、過硫酸ナトリウム等の過酸塩類、ベンゾイルパーオキシド、アゾビスイソブチロニリジン、クメンハイドロパーオキシド等が用いられ得る。

る。この使用量が0.001モル%未満では重合時間や誘導時間が長くなり、また誘導モノマーも多くなり弱く貯ましくない。また従来の重合方法では、誘導モノマー一価樹や誘導期間、重合時間の増加のため、重合開始量を増加させると自己硬化などの不要な反応が起こり吸水率が低下するため、使用できる誘導剤量にも限られてきていたが、本発明の方法によれば、かかる欠点は改善され、開始剤量は増加しても高活性の吸水性樹脂が得られる。しかし2モル%より多く使用しても、添加量に見合った効果が少ないばかりで、重合反応の制御が困難となってしまいますので好ましくない。

本実験で得られる吸水性樹脂は高濃度で重合させると重合熱により乾燥と重合を同時に進行してもよい。重合後の含水率によっては得られた含水率は、重合後に乾燥することによって吸水性樹脂として用いてもよい。乾燥方法としては公知の乾燥装置を用いることが多く、例えは有塩化銅中で乾燥する方法による方法、油類通風炉、真空乾燥機、マイクロ波乾燥機等、所定温度に加熱を加えて乾燥させる方法である。

アサリド等のハイドロロバリオキサイド；2,2'-アゾビス（2-アミジノプロパン）二塩酸塩等のアゾ化合物；その他、第二セリウム塩、過マンガン塩等が挙げられる。中でも得られる吸水性樹脂の性能面や分解生成物の安全性等の点から、過硫酸塩、過酸水素、アゾ化合物よりなる群から選ばれる1種または2種以上が好ましい。

またラジカル重合開始剤が酸化性ラジカル重合
開始剤の場合、還元剤を併用してレドックス系開
始剤として用いても良い。用いられる還元剤とし
ては、例えば亜硫酸ナトリウム、亜硫酸水素ナト
リウム等の亜硫酸（水系）塩；チオ硫酸ナトリウ
ム等のチオ硫酸塩；重二チオン酸塩；硫黄第一陰
イ온のチオ硫酸塩；重二チオン酸塩；硫黄第一陰
イ离子のチオ硫酸塩；チオ硫酸第一陰イオン等。
有機還元剤：アニリン、モノエタノールアルミン

の還元作用が認められる。

ラカール重合開始剤の使用量は広い範囲とすることであるが、通常、単量体(A)に対して0.001~2モル%の範囲とするのが好ましく、更に好ましくは0.01~0.5モル%の範囲である。

熟されたペルトまたはドラムドライヤー等を用いる乾燥方法が挙げられる。これらの乾燥方法を用いる、重合体の含水率が80%以上で、より好ましくは80~230℃で乾燥することが好ましい。80℃では乾燥に時間がかかり生産性の点から好ましくない。また230℃で乾燥し、吸水率の劣化が原因となる場合がある。乾燥を要する

また以上のように配合、乾燥して得られたたばこ吸水性
問題は、必要により防湿およびたばこは分級して使
用される。

さらに本発明は、前記製造方法によって得られる塩水性樹脂(D)の表面近傍を特定の塩水性樹脂類(E)で充填させた塩水性樹脂(F)の製造方法をも提供する。本発明の前記製造方法によって得ら

従来の吸水性樹脂に比べて著しい吸水特性の改善効果を示し、表面近傍を乾燥した吸水性樹脂(4)には表面近傍を乾燥する前の吸水性樹脂(3)に比べて、さらに耐久性に優れた吸水特性に優れたもの

(実施例)

以下、実施例により本発明を説明するが、本発明の範囲はこれらの実施例にのみ限定されるものではない。尚、実施例に記載の吸水性樹脂の量は下記の実験方法によって測定した値を示す。また、部は重量部を示す。

(1) 生理食塩水の吸水倍率

吸水倍率 $(g/g) = \frac{\text{乾燥ゲルの重量}}{\text{乾燥ゲルの乾重}}$
 塩化ナトリウム水溶液中の入ったビーカーに浸漬し、ゆっくりマグネチックスターラーで攪拌した。8時間後に乾燥ゲルを金網で濾過し、十分に水切りをした後の乾燥ゲルの量を測定し、以下の式で吸水倍率を算出した。

$$\text{吸水倍率 (g/g)} = \frac{\text{乾燥ゲルの重量}}{\text{乾燥ゲルの乾重}}$$

(2) 人尿の吸水倍率

(1) の生理食塩水に代えて、成人男子10人からサンプリングした人尿を用いる以外は同様に行い、人尿での吸水倍率を測定した。

所した。劣化状態の判定は、 $O \sim \Delta \sim x$ の3段階評価とした。

O: 膨潤ゲルの形状が保持されている。
 Δ : 一部、膨潤ゲルの形状が崩れている。
 x: 膨潤ゲルの形状が崩れ、ドロドロの流動状となっている。

(6) もどり量

上記膨潤ゲルの耐久試験後に用いた18時間後の子供用オムツの不織布の上に2つ折りにした23cc \times 23ccのペーパータオルを10枚かぶせ、40g/cc \times の圧力を1分間かけてペーパータオルに戻ってきた量の量を測定した。

(7) 膨潤ゲルのベトツキ

(1) で吸水倍率を測定した後の膨潤ゲルのベトツキ (ドライ感) を手触りにて判定した。ドライ感の判定は、 $O \sim \Delta \sim x$ の3段階評価とした。
 O: 膨潤ゲルははかりナラサラサラしてドライ感がある。

Δ : 一部、膨潤ゲルがベトツキ。
 x: 膨潤ゲルがベトツキ、手がスベスベしている。

(3) 水可溶分

吸水倍率0.5gを100.0mlの脱イオン水中に分散し、12時間後、濾紙で濾過し、濾液中の固形分を測定して次式に従って水可溶分を求めた。

$$\text{水可溶分 (\%)} = \frac{\text{濾液の重量 (g)} - \text{濾液の固形分 (g)}}{0.5 (\text{g})}$$

(4) 水可溶分の分子重

分子重が既知の固形のポリアクリル酸ナトリウムを標準にして、ゲルパーミエーションクロマトグラフィーによって、(3) の方法でサンプリングした水可溶分の分子量を求めた。

(5) 膨潤ゲルの耐久性

不織布、綿状バルブ、吸水紙および防水フィルムからなる市販の子供用オムツ (重量72g) を半分に切り、ポリマー2.5gを綿状バルブと吸水紙の間に均一に散布し、成人の人尿120mlを加えて37℃で放置し、8時間、12時間、18時間後にオムツを開いて中の膨潤ゲルの様子を見る。

る。

(8) 膨潤ゲルの透過性

第1図に示すように内径5.3mmのシヤレールに吸水倍率1.0gを入れ、人尿10mlを注ぎ膨潤ゲル2を挿入する。膨潤ゲル2の上に直径5.3mmのペーパータオル3を置き、更に第1図に示すように、中央に突出した筒状部を有する円板状のアクリル樹脂製試験片4を置く。1時間後に放置した後、人尿6mlを注入口5より注ぎ、人尿が全てポリマー中に吸収されるまでの時間を測定し、それをもって、膨潤ゲルの透過性とする。

(実施例1)

アクリル酸41.4g及びアクリル酸ナトリウム37.7重量%水溶液43.80g、および架橋剤(8)としてトリメチロールプロパントリアクリレート6.815g (対単量体(A) 0.1モル%)、水溶性連鎖移動剤(C)として次亜硫酸ナトリウム1水和物0.195g (対単量体(A) 0.008モル%)、イオン交換水670gを用いて温度37℃、中和率75%の単量体水溶液を得た。

(実施例2)

実施例1に於て、用いられる水溶性連鎖移動剤(C) 次亜硫酸ナトリウム1水和物の使用量を、21.9g (対単量体(A) 0.05モル%) とする以外は同様に行い、吸水倍率(2)を得た。

(実施例3)

この吸水倍率(2)を同様に行い、結果を第1表に示す。

(実施例4)

実施例1に於て、用いられる架橋剤(8)をポリエチレングリコールジアクリレート (n=8) とする

以外は同様に行い、吸水倍率(2)を得た。

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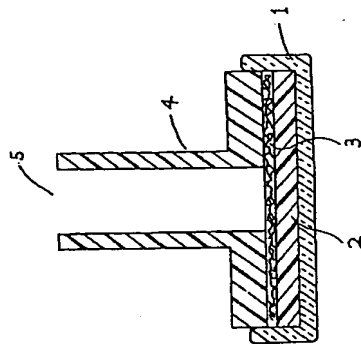
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4. 図面の簡単な説明

第1図は膨潤ゲルの透過性試験器具を示したものである。

- 1 ... シヤーレ
- 2 ... 膨潤ゲル
- 3 ... ペーパータオル
- 4 ... アクリル樹脂製試験筒
- 5 ... 注入口



特許出願人 日本触媒化学工業株式会社

第1図

第1頁の続き

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